# Intensified Bioleaching of Copper from Chalcopyrite: Decoupling and Optimization of the Chemical Stage

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ABSTRACT: A one-stage process for the bioleaching of copper from chalcopyrite has a low leaching rate compared to the conventional smelting, pressure oxidation, and roasting routes, thus reducing the economic viability of the process. It is, therefore, crucial to optimize the process and the associated rate-influencing factors to make it competitive with the traditional, proven technologies. A strategy to intensify the extraction process is the decoupling of the chemical and biological stages, which expands the attainable region for the optimization of the variables. In the present research, the decoupled optimization of the chemical stage in the copper bioleaching of a chalcopyrite ore from the Iranian Sungun mine at East Azerbaijan was investigated. The factors affecting the rate of oxidation of chalcopyrite were determined and optimized with a (realistic) priori prepared bio-related medium. The optimized variables included the reaction temperature of 70 °C, the ore particle size of 0.65 µm, pH of 1.8 in the leaching solution, ferric ion concentration of 0.1 of the stoichiometric value (0.0022 mol per gram of chalcopyrite), and redox potential ~406 mV. Overall, the effect of redox potential on the extraction rate was the most pronounced such that the leaching rate was increased by about three times in the potential range of 401.0–405.8 mV relative to other ranges.

**KEYWORDS:** Process optimization; Bioleaching; ferrous sulfate; Chalcopyrite; Copper sulfide.

## INTRODUCTION

Bioleaching of sulfide minerals is a proven technique that relies on the potential of acidophilic bacteria to extract different metals, such as gold, copper, cobalt, etc. [1-3]. As the bioleaching technology is apt for the pre-treatment of refractory ores, similar processes are being developed for inferior nickel sulfide ores [4]. The bioleaching technologies offer several perceived advantages including (1) operation under atmospheric pressure and ambient

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temperature conditions, (2) the use of naturally occurring components including microorganisms, water, and air, and (3) less harmful environmental impacts due to the absence of dust and SO<sub>2</sub> emissions [5-6]. Moreover, the bacterial leaching technologies have more straightforward operating procedures and lower energy consumption with moderate capital investments and lower operating costs compared to the conventional routes, such as smelting, pressure oxidation, and roasting [5, 7-8].

The bioleaching of sulfide minerals can proceed through two independent steps [2, 9]. As shown in Fig. 1(a) and the equations presented in the following, the reaction mechanism involves the chemical leaching by ferric iron which is reduced to ferrous iron, and the subsequent oxidation to ferric iron under the effect of microorganisms [2]. At the same time, the microorganisms oxidize sulfur to sulfate species and generate sulfuric acid (Eqs. (1) and (2)).

$$4Fe^{2+} + 4H^{+} + O_{2} \rightarrow 4Fe^{3+} + 2H_{2}O$$
 (1)

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$
 (2)

Hence, the extraction of the desired metal species from mineral sulfides such as chalcopyrite is an oxidative reaction in which the sulfide compound of the mineral is converted into the elemental sulfur and metal oxide in the presence of ferric ions acting as oxidant (Eq. (3)) [7].

$$CuFeS_2 + 4Fe^{3+} \rightarrow 5Fe^{2+} + Cu^{2+} + 2S^0$$
 (3)

costs associated with the preservation of microorganisms for sulfide bioprocessing are known to be significantly small as the microorganisms acquire energy from the redox reactions and consume O<sub>2</sub> and the open-air CO<sub>2</sub> (the primary greenhouse gas) as the source of carbon, while obtaining the required phosphorus, nitrogen, potassium and micronutrients from the bioleach environment [7]. The bioleaching process is therefore particularly relevant to climate change mitigation. The main downside of bioleaching from sulfide minerals which often obstructs its commercial application [10] is apparently the slow kinetics of the reactions compared to the other extraction methods, such as pyrometallurgical and other hydrometallurgical approaches [7]. For any competitiveness, the process needs to be optimized with respect to the influencing parameters [8]. A solution for this drawback is suiting and optimizing the biological and chemical sub-processes independently [10]. In a broader sense, the process decoupling is critically important for several reasons. For instance, although high temperatures favor the operation at the chemical stage, it is detrimental or even fatal to the microorganisms. Analogously, while vigorous mixing is beneficial in the chemical section, it can gradually remove the biofilm formed on the mineral particles in a one-pot scenario. The third incentive is the fact that ultrafine particles that accelerate leaching can decrease the effectiveness of biofilm conservation and increase the possibility of a carryover of microorganisms within the effluent stream.

Fig. 1(b) demonstrates an illustrative overview of such a decoupling scenario for a copper extraction process. Accordingly, one can prevent an unfavorable interference of the parameters in the two sub-processes and their negative impacts on the reaction rate. In the chemical stage, the ferric ions generated in the biological stage oxidize the chalcopyrite mineral and release the copper ions.

Chalcopyrite is among the most important yet challenging minerals to leach and, therefore, considerable efforts have been devoted to delineating the mechanism for the oxidative leaching of copper from this mineral [11]. A comprehensive literature survey uncovers several factors that influence the chalcopyrite oxidation rate: temperature, chalcopyrite particle size, solution pH, concentration of the ferric ion, redox potential between the leaching medium and the surface of mineral, density of dislocations in crystalline aggregates, and type of mineral impurities, with the last two ones originating from the mine itself. The dependence of the leaching rate upon the ore properties requires that the optimum conditions of bioleaching are determined for every source of chalcopyrite.

Owing to the essential advantages of the biological extraction in a decoupled scheme and the lacking information on the Iranian mines, on the one hand, and the necessity of mine-tailored optimizations, on the other hand, the bioleaching of copper from a chalcopyrite mineral from East Azerbaijan of Iran was investigated for the first time in the present study. Unlike previous attempts, the present study was based on applying a realistic solution in the optimization of the chemical stage, being as close to the culture medium employed in the biological stage as possible. More particularly, the influencing parameters in the chemical sub-process including temperature, chalcopyrite particle size, pH

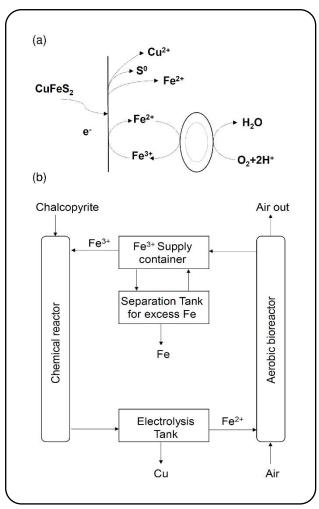


Fig. 1: (a) Different microbial roles in the coupled bioleaching of copper and sulfide minerals [7], and (b) a schematic diagram of the two-step bioleaching process for extraction of copper from chalcopyrite.

of the leach solution, redox potential between the solution and mineral surface, and ferric ion concentration were optimized altogether. We are unaware of such a multidimensional optimization study for Iranian chalcopyrite or even from other mines.

### EXPERIMENTAL SECTION

# Materials and Reagents

All tests were implemented with the chalcopyrite mineral (approximately 56% CuFeS<sub>2</sub> or ~19% Cu) obtained from the Sungun mine, East Azerbaijan, Iran. Pretreatment was implemented using a pulverizer. The average particle size of the minerals in all experiments, except for the tests on the effect of particle size, fell into

the range of 0.39–0.99  $\mu m$  (as found from the DLS data), with the mean effective size of 0.65  $\mu m$ .

Following the reaction stoichiometry, 3.05 g/L of ferric sulfate [Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (80% purity)] was employed for every 1 g/L of chalcopyrite (with a 56% purity). The ferric concentration was kept the same in all of the experiments except those on the effect of this variable. In all runs except those requiring the change in the variable, the pH of the solution was adjusted at 1.8 (the optimum value for the effluent of the biological sub-process) using sulfuric acid. All experiments except those on the effect of temperature were controlled at 70 °C. Taking into account that the ferric concentration was kept constant, varying amounts of ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) were added to the solution to probe the effect of redox potential. The selected conditions of the leaching solution were based on the Eh-pH diagrams reported elsewhere [12]. In the two-stage extraction process, the leach solution employed in the biological stage, which contains nutritious salts for the bacteria enters the chemical stage. To mimic the real conditions, therefore, 0.4 g/L of the constituents of the culture medium, including KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were also introduced into all of the solutions.

## Characterization apparatus

Field emission scanning electron microscopy (FESEM) was implemented on a MIRA III, TESCAN instrument. The X-ray powder diffraction pattern was obtained using a PHILIPS, PW1730 apparatus. Dynamic light scattering (DLS) analysis was performed on BROOKHAVEN, OMNI instrument. The redox potential and pH were measured on a Consort C3020 multimeter where the redox probe was a Mettler-Toledo InLab redox Pro electrode and the pH probe was a Consort SP10T electrode. The X-Ray Fluorescence (XRF) analysis was performed on a SPECTRO XEPOS spectrometer.

#### Leaching tests

All of the leaching runs were performed in 1000 mL flasks containing 1 g of chalcopyrite under stirring at 1100 rpm. Periodically, samples of 30 mL volume were taken from the reaction solution to evaluate the reaction kinetics. The copper concentrations of the samples were measured using atomic absorption spectroscopy.

Component	Value (%)	Component	Value (%)	Component	Value (%)
Na <sub>2</sub> O	7.000	V	0.003	Zr	0.007
MgO	2.036	Cr	0.006	Мо	0.003
$Al_2O_3$	2.007	Mn	0.067	Ag	0.014
SiO <sub>2</sub>	9.901	Fe	16.980	Sn	0.007
$P_2O_5$	0.001	Ni	0.006	Sb	0.006
$SO_3$	34.170	Cu	19.41	Те	0.005
Cl	0.086	Zn	0.085	I	0.003
K <sub>2</sub> O	0.082	Rb	0.001	Ta	0.242
CaO	6.225	Sr	0.027	W	0.041
TiO <sub>2</sub>	0.313	Y	0.002		

Table 1: Composition list of the investigated chalcopyrite mineral obtained from XRF analysis.

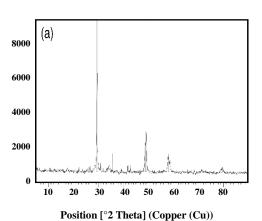
series of experiments were designed to explore the effects of operating variables. These variables were temperature, particle size, solution pH, initial ferric ion concentration, and redox potential. In the leaching tests to study the effect of the redox potential, the potential was additionally evaluated such that the extent of leaching at different time intervals and potential ranges could be compared against similar experiments. A final test was also implemented with all variables at their optimal values.

#### RESULTS AND DISCUSSION

The chemical composition of the investigated mineral has been tabulated in Table 1. As evident, the predominant elements in the Sungun chalcopyrite were Cu, Fe, S, Na, Ca, and Si, respectively. The X-Ray Diffraction (XRD) analysis (Fig. 2) showed the presence of a highly purified chalcopyrite as the dominant phase along with minor amounts of quartz and magnetite phases. Observation of the sample by FESEM revealed that the Sungun ore was composed of lots of small flakes of irregular morphology and several aggregated particles of sharp-edged quadrilateral boxes with relatively smooth surfaces (Fig. 2). In the following, we discuss the results obtained from the experimental optimization of the chemical sub-process for the oxidation of the Sungun chalcopyrite using the ferric ions from the biological stage.

## Effect of temperature

Temperature is an essential factor that affects the leaching rate of chalcopyrite. More precisely, the kinetics



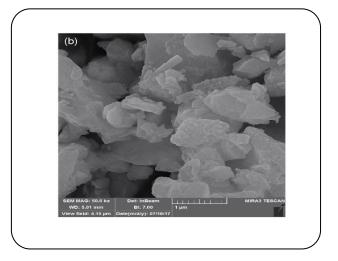


Fig. 2: XRD pattern (a) and FESEM images (b) of the chalcopyrite ore used in this work.

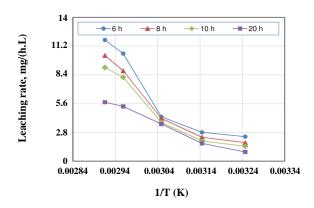


Fig. 3: Effect of temperature on the leaching rate of chalcopyrite at pH of 1.8, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 3.05 g/L, the particle size of 0.65 µm, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

of chalcopyrite dissolution and hydrolysis of ferric ions are very slow at low temperatures. An increase in temperature is, therefore, positive in terms of chalcopyrite dissolution and increasing the oxidation rate [13]. On the other hand, the rate of ferric ion hydrolysis increases at elevated temperatures, thus diminishing the oxidation rate. For the effect of temperature, the extents of copper extraction were investigated in the temperature range of 35–70 °C. Fig. 3 shows the variation of the Sungun chalcopyrite leaching rate with the reaction temperature at different extraction times. The results indicated that an increase in the extraction temperature while keeping the other parameters constant, increases the chalcopyrite oxidation rate.

The effect of temperature on the amount of extracted Cu as a function of contact time is shown in Fig. 4. As indicated in these plots, the effect of temperature was linear between 45–65 °C such that the extraction rate was increased by more than 2.5 times upon increasing the reaction temperature from 45 to 65 °C. The activation energy within this range was estimated to be about 81.6 kJ/mol at the initial time interval, which may be compared to the activation barriers reported by other researchers, e.g., 71 kJ/mol [14], 84 kJ/mol [15], 88 kJ/mol [16], and 130.7 kJ/mol [13]. At the temperatures outside this range, the slope of changes was comparably low.

Most of the previous studies have emphasized the decisive role of temperature on the extraction rate [16]. For instance, Cordoba et al. achieved the highest amount of extraction (ca. 86%) at the highest

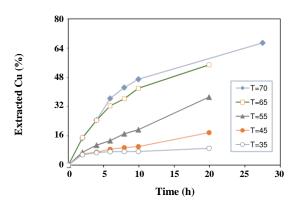


Fig. 4: Effect of temperature on the extraction amount of Cu (with respect to the initial 194 mg per 1 L) at different reaction times at pH of 1.8, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 3.05 g/L, particle size of 0.65 µm, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

temperature investigated (68 °C) over 13 days at a pulp density of 0.5%, initial redox potential of 400 mV, and the total iron concentration of 5 g/L [13]. In spite of the different operating conditions employed in the present study, high extraction amounts were obtained within 24 h. A comparison of this estimate with the 13 days reported by Cordoba et al. indicates the substantially high extraction rate in the present study.

## Influence of particle size

The oxidation rate of chalcopyrite is evidently dependent upon the particle size of mineral such that the rate of leaching is accelerated upon a decrease in the size of particles [11]. Fig. 5 demonstrates the extraction rate of copper for different chalcopyrite particle sizes, varying from about 0.65 μm to 1 mm. The other variables (temperature, pH of the leach solution, ferric ion concentration and redox potential) were kept unchanged for obtaining these data points. Fig. 5 indicates that the decrease in particle size increased the reaction rate substantially. In fact, the decrease in the particle size increases the specific surface area available for leaching and therefore the effective contact with the oxidizing agent and finally, the leaching rate [7]. We note, however, that the pronounced effect of the increased surface area turns into a plateau at extremely large surface areas. This observation is in agreement with previous reports of dichromate leaching of chalcopyrite, which indicated that that the impact of increasing the dislocation density and mineral impurities on the oxidation rate

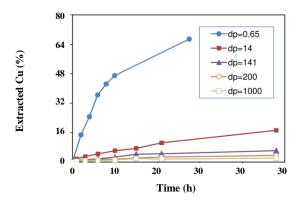


Fig. 5: Effect of chalcopyrite particle size on the extraction amount (with respect to the initial 194 mg per 1 L) at the temperature of 70 °C, pH of 1.8, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 3.05 g/L, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

was intensified at large chalcopyrite particles [14]. Whereas no clear alteration in the extracted amount was observed in the range of 0.10–0.14 mm of mineral, a further decrease in the particle size led to an abrupt increase in the extracted copper. As evident, the highest amount of extracted copper was 129.8 mg (66.87%), which was obtained after 27.5 h with the effective mineral particles of 0.65  $\mu$ m mean size. This finding is in accordance with the results of *Pinches et al.* [17] who investigated the effect of particle size of chalcopyrite from a North American mine at the constant operating parameters of 70 °C, the initial redox potential of 434 mV and pH of 1.5. Within a 48 h period, they observed that the extraction amount increased from 40% to 98% upon a decrease in the chalcopyrite particle size from 103.8 to 6.9  $\mu$ m.

#### Influence of pH

To probe the effect of pH, the magnitude of extracted copper was measured at different pH levels in the range of 1.5–2.2 with respect to time (shown in Fig. 6). As apparent in this figure, the optimal pH of the solution was found to be 1.8, which is tantamount to the ideal pH of the effluent from the biological stage of the process. At higher and lower pH levels, the oxidation rate was reduced. A relatively lower value of 1.5 was obtained for another mine by Halinen et al. [4] who studied both the biological and chemical stages in the same container. In another work, Antonijević and Bogdanović [18] reported their highest extraction (0.116 g/L) at a slightly higher pH of 2.0 in 90 days. As a general remark, the more acidic the solution

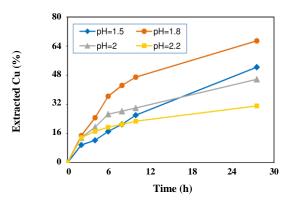


Fig. 6: Effect of pH of the solution on the leaching amount (with respect to the initial 194 mg per 1 L) at the temperature of 70 °C, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 3.05 g/L, particle size of 0.65 μm, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

(e.g., in the range of 0.5–2.0), the less likely the hydrolysis and precipitation of the ferric salts [14]; even though, some authors reported poor dissolution of chalcopyrite at low pH levels [18-19]. The leaching of chalcopyrite is itself an acid consumption reaction. In contrast, at high pH levels and high concentrations of ferric ion, iron hydroxide species, predominantly the jarosite will precipitate. This, in turn, prevents from effective contact of the oxidant with chalcopyrite and, hence, inhibits the oxidation rate.

#### Effect of redox potential

The effect of redox potential on the dissolution rate of the Sungun chalcopyrite was investigated at the optimum temperature of 70 °C and the optimal pH of 1.8. The investigated levels of the initial redox potential were 373.3, 402.7, 405.8, 415.2, 418.0, 422.6, 431.4, 437.8, 452.0, and 481.5 mV. As the redox potential was not controlled as a set point in the experiments and only the potential of the samples was measured, the amounts of extracted copper could determine the effect of the redox potential on the rate of leaching from the Sungun chalcopyrite. In addition, as all solutions had identical conditions at the initial time except for their different potentials, the extraction amount in the first hour is particularly essential. As indicated by Fig. 7, the highest measured extraction amount was 82%, which was accomplished at the redox potential of 452.0 mV. Concerning the initial leaching rate, however, the most favorable potential difference was 405.8 mV. After 1 h,

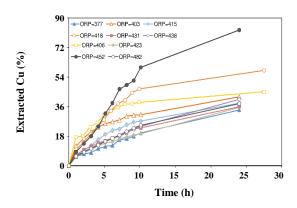


Fig. 7: Influence of the redox potential on the leaching amount (with respect to the initial 194 mg per 1 L) at the temperature of 70 °C, pH of 1.8, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 3.05 g/L, particle size of 0.65 μm, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

this potential was reduced to 401.0 mV where the extracted amount was 34 mg of copper, which exceeds 17.5% of the total Cu content of the sample. One may conclude that the effect of redox potential on the rate of copper leaching from chalcopyrite is of extreme importance. In particular, the rate of extraction at 401.0–405.8 mV was almost 3 times those at other intervals for the same sample. In other words, if the redox potential is kept at ~406 mV with a ferric ion makeup, the extraction rate will be preserved at ~34 mg/(L·h), which is a high leaching rate.

leaching process is, in essence, electrochemical event; hence, one would expect that the oxidation rate depends on the potential difference between the chalcopyrite surface and the solution [11, 20-22]. During the extraction, the surface of chalcopyrite has to be exposed to the leaching solution and, particularly, the oxidant component (Fe<sup>3+</sup> ion) [7]. In some instances, the solid products can accumulate at the interface of mineral and leach solution, thus retarding the extraction [11]. The extent of the solid precipitates depends on the redox potential and pH of the solution. An immediate consequence of high potential in the solution of monovalent alkali cations and sulfate ions is that the ferric ions readily solidify as a basic sulfate, e.g., the jarosite [MFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] as represented in Eq. (4).

$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O_2 + M^+ \rightarrow$$

$$MFe_3(SO_4)_2(OH)_6 + 6H^+$$
(4)

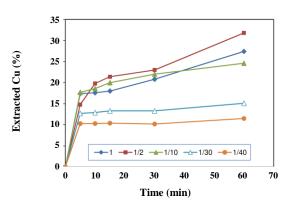


Fig. 8: The dependence of the leaching amount (with respect to the initial 194 mg/L) on the ferric concentration at the temperature of 70 °C, pH of 1.8, particle size of 0.65  $\mu$ m, and 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

in which M<sup>+</sup> is K<sup>+</sup>, Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup>. The iron sulfate precipitates form a passivating layer that impedes the complete dissolution of chalcopyrite. This passivation interferes with the transportation of both ion species and electrons between the mineral particles and the leaching solution, thus retarding the oxidation of chalcopyrite [13].

The difference between the optimum values of the redox potential obtained in the present study and that by some other investigators [17] can be explained by the different types of chalcopyrite minerals and the other influencing factors. However, the differences between the applied parameter ranges and the disparities of the physicochemical properties of the investigated minerals prevent a more comprehensive comparison of the results against the previously published data. This also necessitates customized optimization studies for different sources of chalcopyrite, here from the Sungun mine.

## Effect of ferric ion concentration

As noted previously, the precipitation and nucleation of jarosites from iron hydroxide species over the mineral particles leads to the passivation of chalcopyrite. This occurs mainly at the basic conditions and high ferric ion concentrations [7]. The variation of leaching rate with concentrations of ferric ion is shown in Fig. 8. In these experiments, we decided to consider only the alterations of the concentration of Fe<sup>3+</sup> ions rather than the total iron concentration, which also takes into account the less influencing Fe<sup>2+</sup> ions. From this figure, it is indicated that the optimum ferric ion

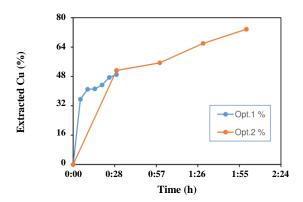


Fig. 9: The extracted amount (mg Cu with respect to the initial 194 mg per 1 L) in terms of reaction time at the optimum conditions at the temperature of 70 °C, pH of 1.8, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O concentration of 0.305 g/L, particle size of 0.65 μm, 0.4 g/L concentrations of KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and the redox potential of 405.8 mV.

concentration with respect to the rate of leaching is one-tenth of the stoichiometric value, i.e., 0.305 g of iron sulfate [Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O] per 1 L of solution. At lower values of ferric ion concentration, their insufficiency reduces the frequency of collisions and, hence, the leaching rate. At concentrations higher than the optimum value, the low dissolution rate of the Sungun chalcopyrite leads to an excess (higher than stoichiometric) amount of ferric ions in the solution, thus leading to the hydrolysis of the excess ions and their nucleation at the mineral surface. This, in turn, passivates the mineral and reduces the rate of copper leaching.

Indeed, the role of ferric ion in the solution is twofold: (1) it assists with the leaching of mineral at appropriate ferric concentrations, and (2) it gives rise to the passivation of the surface at high ferric concentrations. The latter protects the surface from attacks of the intermediates, thus decreasing the oxidation rate of chalcopyrite [23].

## The optimum operational point

The results obtained in the present work indicated that the optimal point in the chemical stage of the copper leaching from the Sungun chalcopyrite minerals is described by the temperature of 70 °C, particles of 0.65 µm mean size, pH of 1.8, ferric ion concentration of 0.1 of the stoichiometric value (0.0022 mol Fe<sup>3+</sup> per gram of chalcopyrite), and the redox potential of 405.8 mV. As the leaching reaction progresses, the redox potential and the ferric ion concentration both reduce away from

the initial values. An additional experiment was therefore conducted at the optimal point in which the sampling was done every 5 min instead of the 30 min intervals.

As all variables are at their optimum values at the onset of leaching, the first and most instantaneous sample taken from the solution is the closest to the optimum reaction rate. As can be seen in Fig. 9, the extraction amount within the first 5 min was about 36% of the total copper in this period. This indicates that the actual initial rate was much higher than that reported with the 30-min sampling. If the ferric ion spent in the first period is to be compensated continuously, the affected parameters such as the redox potential and the ferric concentrations will be held in their favored ranges and, hence, the leaching rate will be kept near the high rate of 82.8 mg/(L·h). As such, all of the Cu content would be extracted within the first 15 min. By comparing the leaching rate at the optimal point with those at the individual optimum levels of the operating parameters with a one-at-a-time approach, one can find out that the leaching rate has been markedly improved at the multidimensional optimized conditions. The improvements are of further significance, taking into account that the factors affecting the oxidation rate were evaluated in a realistic bio-related medium containing nutritious salts appropriate for the bacteria.

The results presented here provide helpful insights into the optimum decoupling of the process at hand. As mentioned previously, the decoupled process has several advantages over a one-pot reaction scheme. For instance, although high-temperature operation (70 °C) is favorable at the chemical stage, it is detrimental to the microorganisms in a one-pot scenario. Analogously, while vigorous mixing (1100 rpm) is beneficial for enhancement of the leaching rate, it can potentially remove the biofilm deposited on the mineral carrier in a one-pot scenario, thus decreasing the total efficiency. Moreover, the ultrafine particles that could accelerate the copper leaching may reduce the effectiveness of the formation and preservation of biofilm on the surface of the mineral with an increased possibility of a carryover of microorganisms with the fluid leaving the vessel. On the other hand, the formation of biofilm on the surface of chalcopyrite in a one-stage process can partially disable the contact of Fe<sup>3+</sup> ions with the surface of chalcopyrite crystals, thus limiting the extraction of copper. The optimized process within a decoupled scheme can circumvent all these limitations.

#### **CONCLUSIONS**

Owing to the negative interconnection of the parameters from the chemical and biological stages of the bioleaching process, these two parts were decoupled for a more convenient and more efficient optimization of the process using the chalcopyrite mineral from the Sungun mine of East Azerbaijan Province of Iran. The results showed that the optimal operating point at the chemical stage of leaching from this mineral is described by the temperature of 70 °C, the chalcopyrite particle size of 0.65 µm, the pH of 1.8, the ferric ion concentration of 0.1 of the stoichiometric value (0.0022 mol Fe<sup>3+</sup> per gram of chalcopyrite), and the redox potential of 405.8 mV between the chalcopyrite surface and the leach solution. The obtained data demonstrated that the separate optimization of the chemical stage undoubtedly leads to the remarkable enhancement of the extraction rate. The highest measured extraction amount was ~82% obtained after 24 h. A comparison of this extraction period with the 13 days reported by Cordoba et al. indicates the substantially high extraction rate in the present study. The improvements are of further significance, taking into account that the factors affecting the oxidation rate were evaluated in a realistic bio-related medium containing nutritious salts appropriate for the bacteria. Owing to the elimination of the interplay of the parameters from the two sub-processes and their negative impact on the reaction rate with the decoupling of the chemical and biological stages, the optimization of the biological stage would be applicable as well and will be the subject of future studies. Upon improving the reaction rate of the bioleaching process within a two-stage scenario, the main drawbacks on a practical commercial application of the biological route will be avoided, thus making the process superior to the conventional methods.

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## REFERENCES

- [1] Breed A.W., Hansford G.S., Modeling Continuous Bioleach Reactors, *Biotechnology And Bioengineering*, **64** (6): 671-677 (1999).
- [2] Bircumshaw L., Changunda K., Hansford G., Rawatla R., Development of a Mathematical Model for Continuous Tank Bioleaching, *The Journal of South African Institue of Mining and Metallurgy*, **106**: 227 (2006).

- [3] Mousavi S.M., Vossoughi M., Yaghmaei S., Jafari A., Copper Recovery from Chalcopyrite Concentrate by an Indigenous Acidithiobacillus Ferrooxidans in an Air-Lift Bioreactor, *Iranian Journal of Chemistry* and Chemical Engineering (IJCCE), 25(3): 21-26 (2006).
- [4] Halinen A.-K., Rahunen N., Kaksonen A.H., Puhakka J.A., Heap Bioleaching of a Complex Sulfide Ore: Part I: Effect of pH on Metal Extraction and Microbial Composition in pH Controlled Columns, *Hydrometallurgy*, **98**(1–2): 92-100 (2009).
- [5] Jonglertjunya W., "Bioleaching of Chalcopyrite", PhD Thesis, University of Birmangham, (2003).
- [6] Roshani M., Shojaosadati S.A., Safdari S.J., Vasheghani-Farahani E., Mirjalili K., Manafi Z., Bioleaching of Molybdenum by Two New Thermophilic Strains Isolated and Characterized, Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 36(4): 183-194 (2017).
- [7] Watling H.R., The Bioleaching of Sulphide Minerals with Emphasis on Copper Sulphides A Review, *Hydrometallurgy*, **84(1–2)**: 81-108 (2006).
- [8] Breed A.W., Dempers C.J.N., Hansford G.S., Studies on The Bioleaching of Refractory Concentrates, The Journal of South African Institue of Mining and Metallurgy: 389 (2000).
- [9] Boon M., Heijnen J.J., Chemical Oxidation Kinetics of Pyrite in Bioleaching Processes, *Hydrometallurgy*, 48(1): 27-41 (1998).
- [10] Long Z.E., Huang Y., Cai Z., Cong W., Ouyang F., Biooxidation of Ferrous Iron by Immobilized Acidithiobacillus Ferrooxidans in Poly(Vinyl Alcohol) Cryogel Carriers, *Biotechnology Letters*, **25**(3): 245-249 (2003).
- [11] Kametani H., Aoki A., Effect of Suspension Potential on the Oxidation Rate of Copper Concentrate in a Sulfuric Acid Solution, *Metallurgical Transactions B*, **16(4)**: 695-705 (1985).
- [12] Garrels R.M., Christ C.L., "Solutions, Minerals, and Equilibria", Jones & Bartlett, Boston (1990).
- [13] Córdoba E.M., Muñoz J.A., Blázquez M.L., González F., Ballester A., Leaching of Chalcopyrite With Ferric Ion. Part II: Effect of Redox Potential, Hydrometallurgy, 93(3-4): 88-96 (2008).
- [14] Dutrizac J.E., Macdonald R.J.C., Lngraham T.R., The Kinetics of Dissolution of Synthetic Chalcopyrite in Aqueous Acidic Ferric Sulfate Solutions, *Transactions* of the Metallurgical Society of AIME, 245: 5 (1969).

- [15] Munoz P.B., Miller J.D., Wadsworth M.E., Reaction Mechanism for the Acid Ferric Sulfate Leaching of Chalcopyrite, *Metallurgical Transactions B*, **10(2)**: 149-158 (1979).
- [16] Hirato T., Majima H., Awakura Y., The Leaching of Chalcopyrite with Ferric Sulfate, *Metallurgical Transactions B*, **18**(3): 489-496 (1987).
- [17] Pinches A., Myburgh P.J., Van Der Merwe C., Process for The Rapid Leaching of Chalcopyrite in the Absence of Catalysts: *US Patent US6277341B1* (2001).
- [18] Antonijević M.M., Bogdanović G.D., Investigation of the Leaching of Chalcopyritic ore in Acidic Solutions, *Hydrometallurgy*, **73(3-4)**: 245-256 (2004).
- [19] Lu Z.Y., Jeffrey M.I., Lawson F., An Electrochemical Study of the Effect of Chloride Ions on the Dissolution of Chalcopyrite in Acidic Solutions, *Hydrometallurgy*, **56(2)**: 145-155 (2000).
- [20] Nicol M., Miki H., Zhang S., The Anodic Behaviour of Chalcopyrite in Chloride Solutions: Voltammetry, *Hydrometallurgy*, **171**: 198-205 (2017).
- [21] Nicol M.J., The Use of Impedance Measurements in The Electrochemistry of the Dissolution of Sulfide Minerals, *Hydrometallurgy*, **169**: 99-102 (2017).
- [22] Nicol M., Zhang S., The Anodic Behaviour of Chalcopyrite in Chloride Solutions: Potentiostatic Measurements, *Hydrometallurgy*, **167**: 72-80 (2017).
- [23] Córdoba E.M., Muñoz J.A., Blázquez M.L., González F., Ballester A., Leaching of Chalcopyrite with Ferric Ion. Part I: General Aspects, *Hydrometallurgy*, 93(3-4): 81-87 (2008).